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(54) AQUEOUS SOLUTION OR AQUEOUS DISPERSION OF COPOLYMER HAVING WATER-REPELLING PROPERTY, ITS PRODUCTION AND AQUEOUS COATING COMPOSITION CONTAINING THE SAME

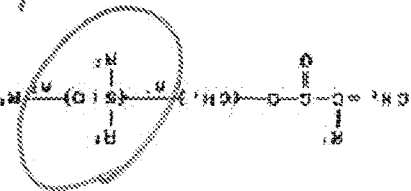
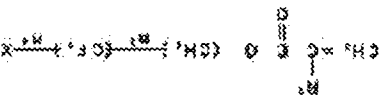
PROBLEM TO BE SOLVED: To obtain the subject aqueous solution useful as a coating resin capable of forming a coating film having

monomer having an alkoxysilyl group, an ethylenic unsaturated

SOLUTION: The objective aqueous solution is produced by

functional group selected from carboxyl group, sulfonic acid group and amino group and (D) 0-95 wt % of other α,β -ethylenic

unsaturated monomers.



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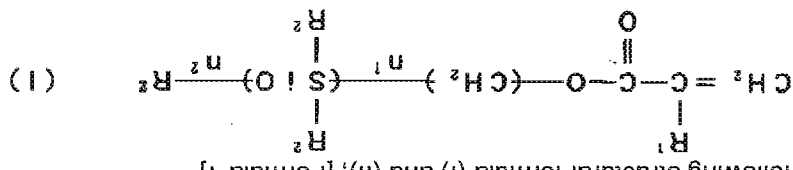
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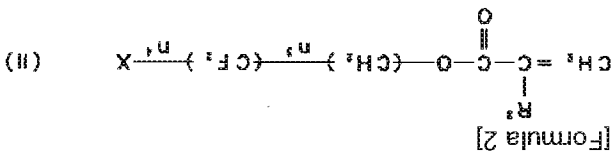
CLAIMS

[Claim(s)]

[Claim 1](a) It is 3 to 70 % of the weight about at least one sort of monomers chosen from a monomer shown by following structural-formula (i) and (ii), [Formula 1]



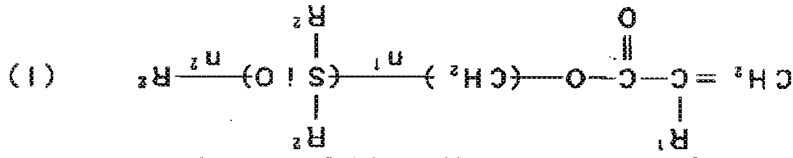
(Among a formula, as for R¹, R² is the same or different in a hydrogen atom or a methyl group, n¹ shows the integer of 1-10 and n² shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers 1-6, respectively.)



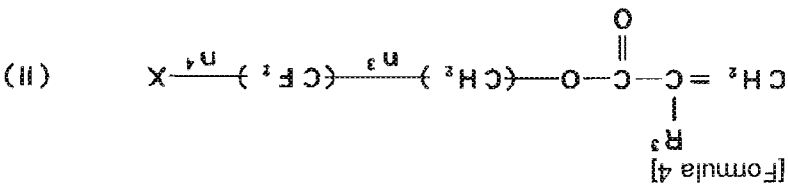
(the inside of a formula, and R³ - a hydrogen atom or a methyl group - X shows a hydrogen atom or a fluorine atom, n³ shows the integer of 1-8, and n⁴ shows the integer of 1-30, respectively.)

The monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has one sort of functional groups chosen from the group of a sulfonic group and an amino group, and beta- ethylenic unsaturated monomer 1 to 25 % of the weight, And the copolymer solution or the water dispersion which has the water repellence carrying out copolymerization of the monomeric mixture which contains alpha in which others are [being (d) and] copolymerizable, and beta- ethylenic unsaturated monomer zero to 95% of the weight.

[Claim 2](a) It is 3 to 70 % of the weight about at least one sort of monomers chosen from a monomer shown by following structural-formula (i) and (ii), [Formula 3]



(Among a formula, as for R¹, R² is the same or different in a hydrogen atom or a methyl group, n¹ shows the integer of 1-10 and n² shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers 1-6, respectively.)



(the inside of a formula, and R^3 — a hydrogen atom or a methyl group — X shows a fluorine atom, n^3 shows the integer of 1-8, and n^4 shows the integer of 1-30, respectively.)

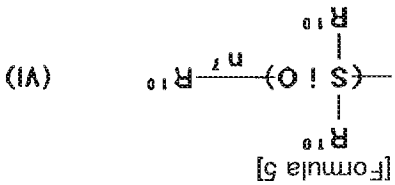
The monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has one sort of functional groups chosen from the group of a sulfonic group and an amino group, and beta-ethylenic unsaturated monomer 1 to 25 % of the weight, And the monomeric mixture which contains 0 to 95 % of the weight for alpha in which others are [being (d) and] copolymerizable, and beta-ethylenic unsaturated monomer, A manufacturing method of the copolymer solution which has the water repellence which adds water and a neutralizer in the copolymer (A) solution produced by performing a radical polymerization in an organic solvent, and is characterized by aqueous-ization or forming moisture powder, or a water dispersion.

[Claim 3] A manufacturing method of the copolymer solution according to claim 2 in which an organic solvent contains alcohol of the carbon numbers 1-8 10% of the weight or more, or a water dispersion.

[Claim 4] After mixing resin (B) solution which does not contain a water-repellent group in a copolymer (A) solution and in which aqueous-izing or water decentralization is possible, water and a neutralizer are added, and it is a manufacturing method of aqueous-izing, the copolymer solution according to claim 2 or 3 formed into moisture powder, or a water dispersion.

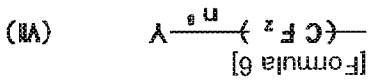
[Claim 5] a copolymer (A) solution — after [or] adding a surface-active agent which has a water-repellent group in a copolymer (A) and a mixed solution of (B) — a manufacturing method of copolymer solution of claims 2 thru/ or 4 aqueous-izing or given in any 1 paragraph which carries out moisture powder, or a water dispersion.

[Claim 6] A manufacturing method of the copolymer solution according to claim 5 whose surface-active agent is what has a water-repellent group shown by following structural-formula (VI), or a water dispersion.



(R^{10} shows a phenyl group or the alkyl group of the carbon numbers 1-6 among a formula, and n^7 shows the integer of 5-200, respectively.)

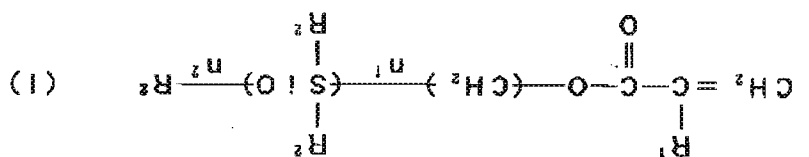
[Claim 7] A manufacturing method of the copolymer solution according to claim 5 whose surface-active agent is what has a water-repellent group shown by following structural-formula (VII), or a water dispersion.



(Y shows a hydrogen atom or a fluorine atom among a formula, and n^8 shows the integer of 1-30, respectively.)

[Claim 8] A manufacturing method of copolymer solution which obtains copolymer solution according to claim 1 or a water dispersion using an emulsion polymerization method, or a water dispersion.

[Claim 9] (a) it is 3 to 70 % of the weight about at least one sort of monomers chosen from a monomer shown by following structural-formula (i) and (ii), [Formula 7]

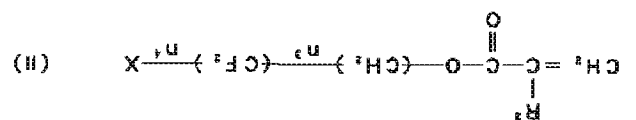


(Among a formula, as for R^1 , R^2 is the same or different in a hydrogen atom or a methyl group, n^1 shows the

integer of 1-10 and n^2 shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers 1-6,

respectively.)

[Formula 8]



(the inside of a formula, and R^3 — a hydrogen atom or a methyl group — X shows a hydrogen atom or a fluorine

atom, n^3 shows the integer of 1-8, and n^4 shows the integer of 1-30, respectively.)

A monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has one sort of functional groups chosen from a group of a sulfonic group and an amino group, and beta- ethylenic

unsaturated monomer 1 to 25 % of the weight, And a distemper constituent which contains copolymer solution or a water dispersion which has the water repellence which carries out copolymerization of the monomeric mixture which contains alpha in which others are [being (d) and] copolymerizable, and beta- ethylenic unsaturated

monomer zero to 95% of the weight as a vehicle component.

[Claim 10]The distemper constituent according to claim 9 in which a monomeric mixture contains a monomer

which has the (e) carbonyl group one to 30% of the weight.

[Claim 11]The distemper constituent according to claim 10 which contains a hydrazine derivative which has at least two -NH-NH₂ content groups in one molecule as a cross linking agent.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to copolymer solution useful as paint resin which can form the coat which was excellent in water repellence and a water resisting property in detail or a water dispersion, a manufacturing method for the same, and the distemper constituent containing this about the copolymer solution or the water dispersion which has water repellence.

[0002]

[Description of the Prior Art] Although the method of giving water repellence to a dry paint film by mixing in paints the water repellent of low molecular weight which is represented by poly dimethylsiloxane was well known from the former, there was a problem of water repellence falling by temporality. On the other hand, it is possible by taking the method of introducing a water-repellent group into resin like a silicone modification acrylic resin to obtain the high water repellent coating film of water-repellent durability.

[0003] Although aqueosity-ization of such water-repellent resin is strongly called for also from on accident

prevention from the field of the health at the time of air pollution prevention and paint, generally conventional

water-repellent resin has strong hydrophobicity, and aqueous-izing and moisture powder are difficult for it. As a means to solve such a problem, the method of aqueosity-izing by carrying out the emulsion polymerization of the alpha and beta-ethylenic unsaturated monomer to an organopolysiloxane macro monomer is indicated, for

example by JP, 2-150475, A. however, a surface-active agent with hydrophilic nature high in this method -- not

using it -- until it does not obtain but sufficient water repellence is shown -- **** -- it did not result. Although there was also a method of carrying out self-emulsification of the water-repellent resin by hydrophilic functional group introduction of a carboxyl group etc., extremely high resin acid value was needed, and it was not able to be said

to be a desirable method from the waterproof field.

[0004]

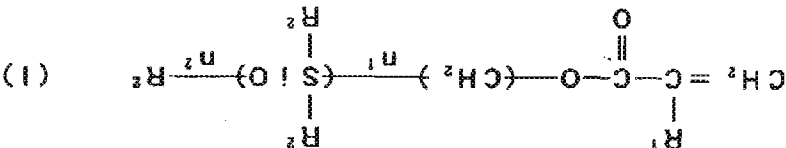
[Means for Solving the Problem] As a result of inquiring wholeheartedly that the above-mentioned problem should be solved, by making indispensable a monomer which has a monomer and alkoxy silyl groups which give water repellence, this invention persons found out that aqueous resin which can give water repellence and a water

resisting property excellent in a coat was obtained, and reached this invention.

[0005] That is, this invention is 3 to 70 % of the weight about at least one sort of monomers chosen from a

monomer shown by structural-formula (I) and (II) of (a) following, [0006]

[Formula 9]



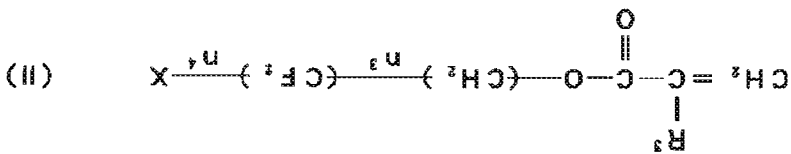
[0007] Among a formula, as for R^1 , R^2 is the same or different in a hydrogen atom or a methyl group, n^1 shows

the integer of 1-10 and n^2 shows the integer of 5-200 for a phenyl group or the alkyl group of the carbon numbers

1-6, respectively.)

[0008]

[Formula 10]



[0009] (the inside of a formula, and R^3 — a hydrogen atom or a methyl group — X shows a hydrogen atom or a

fluorine atom, n^3 shows the integer of 1-8, and n^4 shows the integer of 1-30, respectively.)

The monomer which has alkoxy silyl groups (b) 1 to 40 % of the weight, the (c) carboxyl group, alpha which has

one sort of functional groups chosen from the group of a sulfonic group and an amino group, and beta- ethylenic

unsaturated monomer 1 to 25 % of the weight, And the copolymer solution or the water dispersion which has the

water repellence carrying out copolymerization of the monomeric mixture which contains alpha in which others

are [being (d) and] copolymerizable, and beta- ethylenic unsaturated monomer zero to 95% of the weight, And

the distemper constituent which contains the manufacturing method and this copolymer solution, or a water

dispersion as a vehicle component is provided.

[0010]

[Embodiment of the invention] At least one sort of monomers (a) chosen from the monomer shown by above

structural-formula (i) and (ii) in this invention, Water repellence is given to a copolymer and any 1 way of the

monomer (a-2) containing the fluoride shown by the monomer (a-1) and the above-mentioned structural-formula

(ii) which have a polysiloxane chain shown by the above-mentioned structural-formula (i), or both can be used.

[0011] In the monomer (a-1) shown by the above-mentioned structural-formula (i), although R^1 is a hydrogen atom

or a methyl group and R^2 is a phenyl group or an alkyl group of the carbon numbers 1-6, there is not necessarily

the necessity that it is mutually the same, n^1 — the integer of 1-10, and n^2 — 5-200 — it is an integer of 15-150

preferably. Since the hydrophilic nature of a copolymer runs short and it becomes poor [water solubility or water

dispersibility] when water repellence with n^2 sufficient by less than five is not acquired but it exceeds 200

conversely, it is not desirable. As an example of this monomer (a-1), "Silaplane FM-0711", "Silaplane FM-0721",

"Silaplane FM-0725" (all are the Chisso Corp. make), etc. are mentioned with a commercial item.

[0012] In the monomer (a-2) shown by the above-mentioned structural-formula (ii), R^3 is a hydrogen atom or a

methyl group, and X is a hydrogen atom or a fluorine atom, n^3 is an integer of 1-8 and n^4 is an integer of 1-30. If

n^4 exceeds 30, since mixing nature with other monomers and copolymeric are inferior, and hydrophilic nature

runs short and it will become poor [water solubility or water dispersibility], it is not desirable. as the example of

this monomer (a-2) — 2, 2, and 2-trifluoroethyl (meta-) acrylate, 2,2,3,3-tetrafluoro propyl (meta) acrylate, 2-

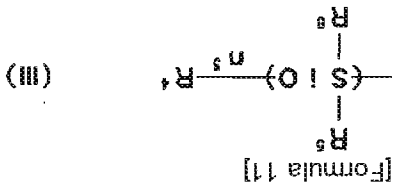
(pentafluoroethyl) ethyl (meta) acrylate, in commercial items, such as 2-(nonadecafluorodecyl) ethyl (meta)

acrylate, "FAMAC" (made by Nippon Mektron, Ltd.), "screw coat 8FM", "screw coat 17FM" (all are the OSAKA

ORGANIC CHEMICAL INDUSTRY, LTD. make), etc. are mentioned.

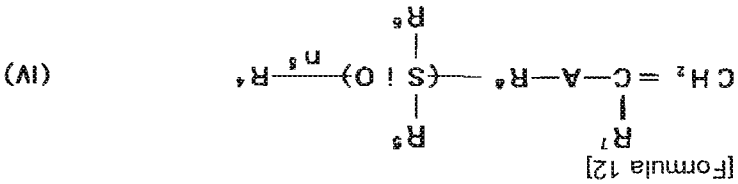
[0013] The monomer (b) which has alkoxy silyl groups in this invention has the alkoxy silyl groups shown by

following structural-formula (iii), [0014]

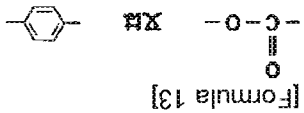


[0015](Among a formula, as for R^5 and R^6 , R^4 is the same or different in the alkyl group of the carbon numbers 1-10, and n^5 shows the integer of 1-4 for a phenyl group, the alkyl group of the carbon numbers 1-6, or the alkoxy group of the carbon numbers 1-10, respectively.) When n^5 is two or more, R^5 comrade and a comrade's R^6 may be the same, or may differ from each other.

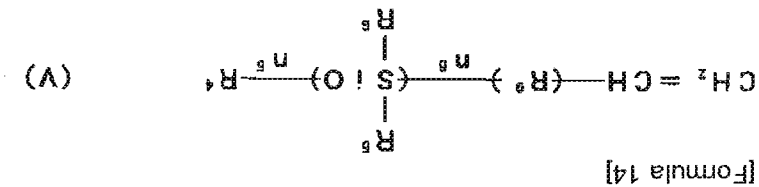
The monomer shown by following structural-formula (IV) and (V) as the example of representation can be mentioned.



[0017](inside of a formula, and A) [0018]



[0019]*****. R^7 shows a hydrogen atom or a methyl group, and R^8 shows the divalent aliphatic-saturated-hydrocarbon group of the carbon numbers 1-6, respectively. R^4 , R^5 , R^6 , and n^5 have the respectively same meaning as the above.

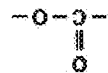


[0021](R^9 shows the divalent aliphatic-saturated-hydrocarbon group of the carbon numbers 1-6 among a formula, and n^6 shows 0 or 1.) R^4 , R^5 , R^6 , and n^5 have the respectively same meaning as the above.

In the above-mentioned structural-formula (IV) and (V), as a divalent aliphatic-saturated-hydrocarbon group of the carbon numbers 1-6 shown by R^8 and R^9 , The alkylene group of a straight chain or the letter of branching, for example, methylene, ethylene, propylene, 1,2-, 1,3- or 2,3-butylene, tetramethylen, ethylethylene, pentamethylene, a hexamethylene group, etc. can be mentioned. As an alkyl group of the carbon numbers 1-6 shown by R^5 and R^6 , The alkyl group of a straight chain or the letter of branching, for example, methyl, ethyl, n-propyl, isopropyl, n-, i-, sec- or tert-butyl, n-pentyl, isopentyl, neopentyl one, n-hexyl, isohexyl, 1-methylpentyl, etc. are mentioned. n-heptyl, 2-ethylhexyl, n-octyl, n-nonyl, n-decyl, etc. other than what was illustrated as an alkyl

group of the carbon numbers 1-6 shown by R^5 and R^6 as an alkyl group of the carbon numbers 1-10 shown by R^4 are mentioned further. As an alkoxy group of the carbon numbers 1-10 shown by R^5 and R^6 , Alkoxy group of straight chain or letter of branching, for example, methoxy, and ethoxy, n -propoxy, isopropoxy, n -, i -, sec - or $tert$ -butoxy, n -pentoxy, isopentoxy, n -hexyloxy, isoheptyloxy, n -octyloxy, etc. are mentioned.

[0022] It is A among monomers of the above-mentioned structural formula (IV). [0023]



[Formula 15]

[0024] Come out and as a certain thing, for example beta-(meth)acryloxy ethoxysilane, gamma-(meta)acryloxypropyl trimethoxysilane, gamma-(meta)acryloxypropyl dimethoxysilane, gamma-(meta)acryloxypropyl methoxydimethoxysilane, etc. can illustrate suitably.

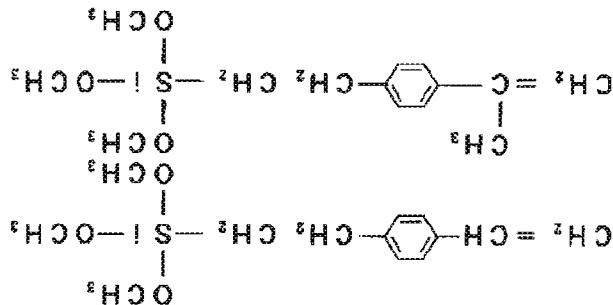
[0025] It is A among the monomers of the above-mentioned structural formula (IV). [0026]



[Formula 16]

[0027] coming out – as a certain thing – for example [0028]

[Formula 17]



[0029] **** is mentioned.

[0030] As a monomer of the above-mentioned structural formula (V), vinyltrimethoxysilane, vinyltriethoxysilane, etc. are mentioned, for example.

[0031] alpha which has one sort of functional groups chosen from a group of a carboxyl group, a sulfonic group, and an amino group in this invention, and beta- ethylenic unsaturated monomer (c), As a monomer which raises water solubility or water dispersibility of a copolymer, and has a carboxyl group, for example (meta), acrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid, 2-carboxyl ethyl (meta) acrylate, 2-carboxyl propyl (meta) acrylate, an unsaturated monomer which has 5-carboxyl pentyl (meta-) acrylate and a hydroxyl group, and anhydrous 2 organic-functions carboxylic acid (for example, a maleic anhydride.) An equimolar addition with itaconic acid anhydride, a succinic anhydride, phthalic anhydride, etc., etc. are mentioned, and 2-(meta) acryloxyethyl sulfonic acid etc. are mentioned as a monomer which has a sulfonic group, for example. As a monomer which has an amino group, they are dimethylaminoethyl (meta) acrylate, diethylaminoethyl (meta) acrylate, and t , for example, - Butylamino ethyl (meta) acrylate etc. are mentioned.

[0032] In this invention, as other copolymerizable alpha and a beta- ethylenic unsaturated monomer (d), For example, methyl acrylate (meta), ethyl acrylate (meta), acrylic acid (meta) n -propyl, (Meta) Acrylic acid isopropyl, acrylic acid (meta) n -butyl, (Meta) Acrylic acid i -butyl, acrylic acid (meta) t -butyl, acrylic acid (meta) hexyl, (Meta) 2-ethylhexyl acrylate, acrylic acid (meta) n -octyl, (Meta) Decyl acrylate, acrylic acid (meta) lauryl, acrylic acid

(meta) stearyl, (Meta) Acrylic acid cyclohexyl, acrylic acid (meta) isobomyl, (Meta) Acrylic acid (meta) ethoxyethyl, (Meta) Acrylic acid (meta) ethoxybutyl, (Meta) Acrylic acid 2-hydroxyethyl, 2-hydroxypropyl acrylate (meta), (Meta) Ester of polyether polyol, such as acrylic acid 3-hydroxypropyl, acrylic acid (meta) 4-hydroxybutyl, a polyethylene glycol, and a polypropylene glycol, and acrylic acid (meta), Which (meta) acrylic ester; Ethyl vinyl ether, n-propylvinyl ether, isopropylvinyl ether, n-butylvinyl ether, t-butylvinyl ether, Hexylvinyl ether, octylvinyl ether, cyclohexylvinyl ether, Vinyl ether, such as phenylvinyl ether, Vinyl acetate, vinyl propionate, Vinyl ester, such as lactic acid vinyl, butanoic acid vinyl, and caproic acid vinyl; Propenyl ester, such as isopropenyl acetate, (Meta) Acrylonitrile, styrene, alpha - Methylstyrene, vinyltoluene, alpha - KURORU styrene etc. are mentioned, and [for the purpose of one sort or two sorts or more], these can be chosen suitably and can be used.

[0033] A copolymerization ratio of the above-mentioned monomers preferably a monomer (a) three to 70% of the weight 5 to 40 % of the weight, it is [monomer / (b)] 20 to 70 % of the weight zero to 95% of the weight one to 25% of the weight in a monomer (c) three to 20% of the weight preferably one to 40% of the weight about 5 to 15 % of the weight, and a monomer (d). Since aqueous-izing of a copolymer or moisture powder-ization will become difficult if water repellence sufficient in less than 3 % of the weight is not acquired but a monomer (a) exceeds 70 % of the weight conversely, it is not desirable. Since it will arise and become easy to gel hydrolysis and a self-condensation reaction of alkoxysilyl groups to a polymerization process of a copolymer, or an aqueous-izing and moisture powder chemically-modified degree if a monomer (b) becomes poor [water solubility or water dispersibility of copolymer aqueous (moisture powder) liquid] in less than 1 % of the weight and exceeds 40 % of the weight conversely, it is not desirable. Since sufficient water repellence will not be acquired but a water resisting property will also fall remarkably further if aqueous-izing of a copolymer or moisture powder-ization becomes difficult and a monomer (c) exceeds 25 % of the weight conversely in less than 1 % of the weight, it is not desirable.

[0034] Copolymer solution or a water dispersion of this invention can be manufactured using a mixture of above-mentioned monomer (a) - (d) by methods, such as an emulsion polymerization method which use a neutralizer and uses aqueous-izing or a method of forming into moisture powder, and ** surface-active agent after ** solution polymerization. From a water-repellent and waterproof point of a coat obtained [especially] by this invention. ** Add water and a neutralizer to this and provide it with a manufacturing method of aqueous-izing, copolymer solution which carries out moisture powder, or a water dispersion, after performing a method, i.e., an above-mentioned monomeric mixture, in an organic solvent, performing a radical polymerization under polymerization initiator existence and obtaining a copolymer (A) solution.

[0035] Copolymer solution or a water dispersion of this invention can be manufactured without using a surface-active agent for water repellence or a water resisting property for an adverse effect according to the manufacturing method of this invention.

[0036] In this invention method, as an organic solvent used at the time of a radical polymerization, it is desirable to be able to use an alcohol system, a cellosolve system, a carbitol system, a cellosolve acetate system, etc., and to contain alcohol of the carbon numbers 1-8 30% of the weight or more especially preferably 10% of the weight or more in an organic solvent. As a radical polymerization initiator, for example 2,2-azobisisobutyronitrile, An initiator of peroxide systems, such as azo polymerization initiators, such as 2,2-azobis (2,4-dimethylvaleronitrile), or lauryl peroxide, t-butyl par 2-ethyl hexanate, and benzoyl peroxide, can be used. This radical polymerization start agent concentration has 0.3 to 10 preferred weight section to monomer 100 weight section.

[0037] In this invention method, as a neutralizer used on the occasion of aqueous-izing or moisture powder, When a monomer (c) has a carboxyl group and a sulfonic group, For example, monomethylamine, dimethylamine, trimethylamine, monoethyl amine, Diethylamine, triethylamine, monoisopropylamine, diisopropylamine, Triisopropyl amine, monobutyl amine, dibutyl amine, tributylamine, Monoethanolamine, diethanolamine,

triethanolamine, Amine, such as dimethylamino ethanol and diethylamino ethanol, When ammonia, sodium hydroxide, a potassium hydrate, etc. can be used and a monomer (c) has an amino group, organic acid, such as inorganic acid, such as chloride, sulfonic acid, and phosphoric acid, formic acid, acetic acid, propionic acid, trimethylacetic acid, acrylic acid (meta), lactic acid, can be used, for example.

[0038] A copolymer (A) obtained by the above-mentioned radical polymerization Aqueous-izing or when moisture powder is carried out, For example, after neutralizing by adding a neutralizer, agitating a copolymer (A) solution, it is also possible to carry out phase conversion of the copolymer (A) which added water or was neutralized by

adding gradually under water, but, in this case, since hydrolysis and a condensation reaction of alkoxy silyl groups advance quickly and there is a possibility of thickening and gelling, in order to prevent it, it is desirable to perform neutralization and water addition as much as possible for a short time. Although time from neutralizer addition to phase conversion by water changes with a reaction vessel, churning conditions, and ambient temperature, specifically, generally, it is convenient to consider it as less than 10 hours preferably for less than 24 hours. It is

the method of aqueous-izing or the most desirable method of carrying out moisture powder adding water in a copolymer (A) solution, and adding a neutralizer after that, without making the above-mentioned copolymer (A) solution thicken and gel. Since a neutralizer which acts also as a hydrolysis catalyst of alkoxy silyl groups, and

promotes bridge construction is blended after moisture powder according to this method, and a silanol group may exist stably, thickening and gelling can be prevented.

[0039] In this invention method, after mixing resin (B) solution which does not contain a water-repellent group in a copolymer (A) solution and in which aqueous-izing or water decentralization is possible, water and a neutralizer are added, and into this mixture, it can water-grit, or can moisture-powder-ize, and can manufacture into it.

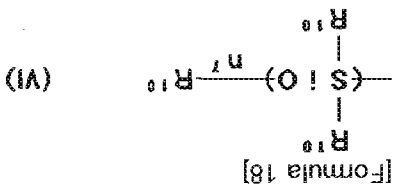
[0040] As this resin (B), if it mixes with a copolymer (A) enough, there will be no restriction in particular. For example, a copolymer obtained by carrying out copolymerization of a monomer which gives water solubility/water dispersibility, and the other monomers, and a copolymer obtained by choosing it as said monomer (c) and a

monomer (b), and (d) suitably from listings, and specifically carrying out copolymerization to them can be used. A copolymerization reaction can be performed like a copolymer (A).

[0041] As for a using rate of resin (B), when using the above-mentioned resin (B), it is preferably desirable in sum total resin solid content with a copolymer (A) to make it become 80 or less % of the weight 95 or less % of the weight. Since sufficient water repellence cannot be acquired if a using rate of this resin (B) exceeds 95 % of the weight, it is not desirable.

[0042] Furthermore, in this invention method, in order to raise water repellence in early stages of coat formation especially on the occasion of aqueous-izing of the above-mentioned copolymer (A), or formation of moisture powder, After adding a surface-active agent which has a water-repellent group in a mixed solution of a copolymer (A) solution or a copolymer (A), and resin (B), it can water-grit or water decentralize.

[0043] As this surface-active agent, what has a water-repellent group shown, for example by following structural-formula (VI) or (VII) can be used.



[0045] R¹⁰ shows a phenyl group or the alkyl group of the carbon numbers 1-6 among a formula, and n⁷ shows the integer of 5-200, respectively.

[0046]

$$[\text{Formula 19}] \quad -(\text{CF}_2)_n\text{Y} \quad (\text{VI})$$

[0047] (V) shows a hydrogen atom or a fluorine atom among a formula, and n^8 shows the integer of 1-30,

respectively.) Specifically as a surface-active agent shown by following structural-formula (VI), polyether modified silicone oil, alkyl modified silicone oil, etc. are mentioned, for example. Specifically as a surface-active agent

shown by following structural-formula (VII), perfluoroalkyl carboxylate, a perfluoro alkyl-sulfonic-acid salt, etc. are mentioned, for example. As for the addition of this surface-active agent, it is desirable that it is 5 or less % of the

weight preferably 10 or less % of the weight to resin solid content. Since the water repellence and the water resisting property of a coat which will be obtained if this addition exceeds 10 % of the weight fall, it is not

desirable.

[0048] On the other hand, by this invention, an emulsifier is used for this through a manufacturing method of the

above-mentioned **, i.e., water, distributed emulsification of the mixture of said monomer (a) - (d) is carried out, and an emulsion polymerization method performed by adding a water-soluble polymerization initiator and heating at

50-90 °C is also provided. If a redox initiator is used, it is also possible to carry out at a room temperature. As an emulsifier, for example Anionic surface active agents, such as sulfate or higher alcohol, and an alkyl-sulfonic-acid

salt, Nonionic surface active agents, such as various alkyl ether of a polyoxyethylene, alkyl ester, and alkyl allyl ether, a reactive surface active agent which has a polymerization nature unsaturation group, etc. are used. As a

polymerization initiator, hydrogen peroxide, ammonium persulfate, cumene hydroperoxide, or a water-soluble

redox initiator is used, for example.

[0049] Subsequently, in this invention, a distemper constituent which contains copolymer solution or a water

dispersion manufactured as above-mentioned as a vehicle component is provided.

[0050] Into a mixture of monomer (a) - (d) used for manufacture of the above-mentioned copolymer solution or a

water dispersion, a monomer (e) which has a carbonyl group can be further contained five to 20% of the weight

preferably one to 30% of the weight if needed from points, such as a water resisting property.

[0051] As a monomer (e) which has a carbonyl group, for example, an acrolein, diacetone acrylamide, die

acetone methacrylamide, Vinyl alkyl ketone, vinyl methyl ketone, vinyl ethyl ketone, vinyl butyl

ketone) etc. which have acetoxymethylmethacrylate, formyl styrol, and 4-7 carbon atoms are mentioned.

Among these [especially], diacetone acrylamide and die acetone methacrylamide are preferred.

[0052] The distemper constituent of this invention can contain a hydrazine derivative which has at least two -NH-NH₂ content groups in one molecule as a cross linking agent, when the above-mentioned carbonyl group is

introduced into a copolymer. Hydrazide groups and a semicarbazide group are contained in a -NH-NH₂ content

group here.

[0053] As this hydrazine derivative, for example Oxalic acid dihydrazide, malonic acid dihydrazide, Glutaric acid

dihydrazide, amber acid dihydrazide, adipic acid dihydrazide, Saturated-fat fellows carboxylic acid dihydrazide

which has 2-18 carbon atoms, such as sebacic acid dihydrazide; Maleic acid dihydrazide; Monoolefin nature

unsaturated-dicarboxylic-acid dihydrazide, such as fumaric acid dihydrazide and itaconic acid dihydrazide;

Phthalic acid, Terephthalic acid or isophthalic acid dihydrazide, and dihydrazide of pyromellitic acid,

TORIHIDORAJUDO or tetrahydrazide; Nit RIROTORI hydrazide, Trihydrazide citrate, 1,2,4-benzene

TORIHIDORAJUDO, ethylene-diamine-tetraacetic acid tetrahydrazide, 1,4,5,8-naphthoic acid tetrahydrazide,

polyhydrazide which makes a low-grade polymer which has a carboxylic acid lower-alkyl-ester group come to

react to hydrazine or a hydrazine hydrate (hydra JINHIDO Iard) (refer to JP, 52-22878, B); Carbonic dihydrazide,

Screw semicarbazide; A polyfunctional semicarbazide produced by making a hydrazine compound and

dihydrazide of the above-mentioned illustration react to a polyisocyanate compound derived from diisocyanate,

such as hexamethylene diisocyanate and isophorone diisocyanate, and it superfluously, A drainage system polyfunctional semicarbazide produced by making dihydrazide of the above-mentioned illustration react to an isocyanate group in a reactant of this polyisocyanate compound and an active hydrogen compound containing hydrophilic radicals, such as polyether polyol and polyethylene-glycols monoalkyl ether, superfluously. Or a mixture (refer to JP, 8-151358, A and JP, 8-245878, A) of this polyfunctional semicarbazide and a drainage system polyfunctional semicarbazide, etc. are mentioned.

[0054] This hydrazine derivative is blended so that 0.01-2 mol of -NH-NH_2 groups in a hydrazine derivative may be 0.05-1.5 mol preferably to 1 mol of a carbonyl group contained in said copolymer solution or a water dispersion. [0055] Further, if needed, additive agents for paints, such as pigments, a bulking agent, aggregate, a pigment agent, a wetting agent, a defoaming agent, a plasticizer, a film formation auxiliary agent, an organic solvent, an antiseptic, an antifungal agent, a pH adjuster, a rust-proofer, and a curing catalyst, can be chosen suitably, can be combined, and can be blended with a distemper constituent of this invention.

[0056] Hereafter, an example is given and this invention is explained still in detail. A "weight section" and "% of the weight" are meant a "part" and "%", respectively. [0057] Isopropyl alcohol 79 weight section was taught into the manufacture example 1 flask of a copolymer water dispersion, and temperature up was carried out, agitating to flowing-back temperature (about 84 °C). Subsequently, the following monomeric mixture was dropped for 4 hours, maintaining temperature at flowing-back temperature. [0058]

Styrene Ten copies 58 copies of n-butyl methacrylate Acrylic acid Seven copies KBM-502 (notes 1) 15 copies Silaplane FM-0711 (notes 2) Ten copies Azobisisobutyronitrile After riping for 2 hours, maintaining at flowing-back temperature after that [one copy], it cools to a room temperature, The almost water-white consistency copolymer solution of 55% of the nonvolatile matter was obtained. Then, the obtained copolymer solution was moved to the dilution tub, after 820 copies of deionized water having added 9.8 copies of triethylamines continuously, carrying out temperature up to 50 °C and performing churning for 2 hours, keeping temperature at 50 °C, it cooled, and the colorless, almost translucent water dispersion of 10% of the nonvolatile matter was obtained. [0059] KBM-502; Shin-Etsu Chemical Co., Ltd. make, an alkoxy-silyl-groups content monomer, Silaplane (notes 2) FM-0711 : (Note 1) In the Chisso Corp. make, a poly dimethylsiloxane group content monomer, and molecular weight 1,000 example 2 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion of 10% of a nonvolatile matter was obtained.

[0060] Styrene Ten copies 28 copies of n-butyl methacrylate Acrylic acid Seven copies Vinyltrimetoxysilane 15-copy Silaplane FM-0711 40 copies Azobisisobutyronitrile In one-copy example 3 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion of 10% of the light opalescence of 10% of a nonvolatile matter was obtained. [0061]

Styrene Ten copies N-butyl methacrylate 58 copies Acrylic acid Seven copies KBM-503 (notes 3) 15 copies Silaplane FM-0725 (notes 4) Ten copies Azobisisobutyronitrile One-copy (notes 3) KBM-503 : [Shin-Etsu Chemical Co., Ltd. make,] An alkoxy-silyl-groups content monomer, Silaplane (notes 4) FM-0725 : In the Chisso Corp. make, a poly dimethylsiloxane group content monomer, and molecular weight 10,000 example 4 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion of 10% of a nonvolatile matter was obtained.

[0062] Styrene Ten copies N-butyl methacrylate 62 copies Acrylic acid Seven copies KBM-502 Ten copies FAMAC (notes 5) Ten copies Azobisisobutyronitrile One-copy (notes 5) FAMAC : [Nippon Mektron, Ltd. make,] The polymerization reaction was performed in the flask by the same operation using the same monomeric mixture as perfluoroalkyl methacrylate and 60.7 % of the weight of fluorine concentration example 5 Example 1, and the almost water-white consistency copolymer solution of 56% of the nonvolatile matter was obtained. Then, the obtained resin solution was moved to the dilution tub, the "KF-355" (Shin-Etsu Chemical Co., Ltd. make, silicone series surface-active agent) 0.4 copy was added, and it agitated for 10 minutes. It cooled, after performing churning for 2 hours, keeping temperature at 50 **, after 820 copies of deionized water having added 9.8 copies of triethylamines continuously after that and carrying out temperature up to 50 **, and the colorless, almost translucent water dispersion of 10% of the nonvolatile matter was obtained.

[0063] The polymerization reaction was performed in the flask by the same operation using the same monomeric mixture as example 6 Example 1, and the almost water-white consistency copolymer solution of 56% of the nonvolatile matter was obtained. Then, the obtained resin solution was moved to the dilution tub, the "Fluorad FC-93" (Sumitomo 3M make, fluorochemical surfactant) 0.15 copy was added, and it agitated for 10 minutes. It cooled, after performing churning for 2 hours, keeping temperature at 50 **, after 820 copies of deionized water having added 9.8 copies of triethylamines continuously after that and carrying out temperature up to 50 **, and the colorless, almost translucent water dispersion of 10% of the nonvolatile matter was obtained.

[0064] Isopropyl alcohol 79 weight section was taught into the example 7 flask, and temperature up was carried out, agitating to flowing-back temperature (about 84 **). Subsequently, the following monomeric mixture was dropped for 4 hours, maintaining temperature at flowing-back temperature.

[0065] Styrene Ten copies 30 copies of n-butyl methacrylate Methyl methacrylate Ten copies Acrylic acid Five copies KBM-502 Ten copies Silaplane FM-071 1 35 copies Azobisisobutyronitrile After riping for 2 hours, maintaining at flowing-back temperature after that [one copy], to a room temperature. It cooled and the almost water-white consistency copolymer solution (A) of 56% of the nonvolatile matter was obtained. In another flask, except having used the following mixture as a dropped monomeric mixture, the polymerization reaction was performed like the copolymer solution (A), and the almost water-white consistency copolymer solution (B) of 56% of the nonvolatile matter was obtained.

[0066] Styrene Five copies N-butyl methacrylate 26-copy methyl methacrylate 37 copies Acrylic acid 2-hydroxyethyl Seven copies Acrylic acid Ten copies KBM-502 15 copies Azobisisobutyronitrile 18 copies of copolymer solutions (A) obtained by the one-copy above like, And after teaching 162 copies of copolymer solutions (B) to a dilution tub, respectively and agitating them for 15 minutes, it cooled, after performing churning for 2 hours, keeping temperature at 50 ** after 816.5 copies of deionized water having added 13.3 copies of triethylamines continuously and carrying out temperature up to 50 **, and the water dispersion of the opalescence of 10% of a nonvolatile matter was obtained.

[0067] The polymerization reaction was performed in the flask by the same operation using the same monomeric mixture as example 8 Example 1, and the almost water-white consistency copolymer solution (C) of 56% of the nonvolatile matter was obtained.

[0068] In another flask, except having used the following mixture as a dropped monomeric mixture, the polymerization reaction was performed like the copolymer solution (C), and the almost water-white consistency copolymer solution (D) of 56% of the nonvolatile matter was obtained.

[0069] N-butyl methacrylate 22 copies Methyl methacrylate 48 copies Acrylic acid 30 copies Azobisisobutyronitrile 108

copies of copolymer solutions (C) obtained by the one-copy above like, And after teaching 72 copies of copolymer solutions (D) to a dilution tub, respectively and agitating them for 15 minutes, it cooled, after performing churning for 2 hours, keeping temperature at 50 ° after 807.1 copies of deionized water having added 22.7 copies of triethylamines continuously and carrying out temperature up to 50 °, and the almost water-white water dispersion of 10% of the nonvolatile matter was obtained.

[0070] 0.15 copy of dodecylbenzenesulfonic acid ammonium and 95 copies of deionized water were taught into the example 9 flask, and temperature up was carried out to 85 °. Then, after using the homomixer for 80 copies of water and distributing the following monomeric mixture, 1.0 copy of ammonium persulfate was added. The water dispersion was dropped into the flask over 5 hours, it was made to ripe for further 2 hours, and the emulsion of the opalescence of 39% of a nonvolatile matter was obtained. The obtained emulsion was diluted with deionized water to 10% of the nonvolatile matter, and was used for system performance testing.

[0071] n-butyl methacrylate 25.5 copies Acrylic acid n-butyl . Copies [50.5] Acrylic Acid 2-Hydroxyethyl 3 Part Acrylic Acid 1 Part Silaplane FM-0711 10 Part KBM-503 10 Part Dodecylbenzenesulfonic Acid Ammonium in 8.7-Copy Comparative Example 1, Although it carried out like Example 1 except having used the following monomeric mixture as a dropped monomeric mixture and the water dispersion was tried with the method of profitably, generation of a coarse particle and sedimentation took place and the good state was not obtained.

[0072] Styrene Ten copies 73 copies of n-butyl methacrylate Acrylic acid Seven copies Silaplane FM-0725 Ten copies Azobisisobutyronitrile in one-copy comparative example 2 Example 1, Although it carried out like Example 1 except having used the following monomeric mixture as a dropped monomeric mixture and the water dispersion was tried with the method of profitably, generation of a coarse particle and sedimentation took place and the water dispersion of the good state was not obtained.

[0073] Styrene Ten copies 73 copies of n-butyl methacrylate Acrylic acid Seven copies Ten copies of FAMAC(s) Azobisisobutyronitrile in one-copy comparative example 3 Example 1, Except having used the following monomeric mixture as a dropped monomeric mixture, the polymerization reaction was performed in the flask by the same operation as Example 1, and the almost water-white consistency copolymer solution of 56% of the nonvolatile matter was obtained.

[0074] N-butyl methacrylate 22 copies Methyl methacrylate 38 copies Acrylic acid 30 copies Silaplane FM-0711 Ten copies Azobisisobutyronitrile The resin solution obtained continuously one copy is moved to a dilution tub, it cooled, after performing churning for 2 hours, keeping temperature at 50 ° after adding 787.8 copies of deionized water, and 42 copies of triethylamines and carrying out temperature up to 50 °, and the almost water-white solution of 10% of the nonvolatile matter was obtained.

[0075] in comparative example 4 Example 1, except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the water dispersion with almost translucent colorlessness of 10% of the nonvolatile matter was obtained.

[0076] Styrene Ten copies N-butyl methacrylate 48 copies Methyl methacrylate 20 copies Acrylic acid Seven copies KBM-502 15 copies Azobisisobutyronitrile Ethylene-glycol-monobutyl-ether 70 weight section is taught into one-copy comparative example 5 flask, Temperature up was carried out agitating to 95 °. Subsequently, the following monomeric mixture was dropped for 4 hours, keeping temperature at 95 °.

Methyl methacrylate 42.5 copies N-butyl methacrylate 12.5 copies Acrylic acid 15 Part Acrylic acid 4-hydroxybutyl 30 Part Azobisisobutyronitrile After riping for 2 hours, keeping temperature at 95 ° after that [0.7 copy], it cools to a room temperature, After adding 21 copies of triethylamines as a neutralizer, it diluted with 45 copies of ethylene glycol monobutyl ether, and the almost water-white consistency resin solution of 43% of the nonvolatile matter was obtained. The obtained resin solution was diluted with deionized water to 10% of the nonvolatile matter, and was used for system performance testing.

[0078] 0.15 copy of dodecylbenzenesulfonic acid ammonium and 95 copies of deionized water were taught into the comparative example 6 flask, and temperature up was carried out to 85 °. Then, after using the homomixer for 80 copies of water and distributing the following monomeric mixture, 1.0 copy of ammonium persulfate was added. The water dispersion was dropped into the flask over 5 hours, it was made to ripe for further 2 hours, and the emulsion of the opalescence of 39% of a nonvolatile matter was obtained. The obtained emulsion was diluted with deionized water to 10% of the nonvolatile matter, and was used for system performance testing.

[0079] Acid 1 Part Siliplane FM-0711 20 Part Dodecylbenzenesulfonic Acid Ammonium Water Dispersion or Solution of Examples 1-9 and Comparative Examples 3-6 Obtained as 8.7-Copy System-Performance-Testing above, All show good water dispersibility.

These were painted by a 50-micrometer applicator to the glass plate, respectively, and after making it dry at 100 ° for 2 hours, the following system performance testing was presented.

A result is shown in Table 1.

[0080](*) Paint film appearance : viewing estimated and O and a gloss ***** private seal **** thing were made into x for the good thing.

[0081](*) Water repellence : the waterdrop of 0.03 cc of deionized water was formed on each coated plate, and the angle of contact of waterdrop was measured with the harmony chemicals company make KONTAKU tongue gurn meter DCCA type. It is shown that water repellence is so good that the numerical value of an angle of contact is large.

[0082](*) Water resisting property : after ****(ing) each coated plate to 20 ** waterworks for 6 hours, what O, a white bluish mark, and blistering are accepted to in what does not have abnormalities in the painted surface was made into x.

[0083] [Table 1]

	実施例										比較例	
	1	2	3	4	5	6	7	8	9	3	4	5
塗膜外觀	○	○	○	○	○	○	○	○	○	○	○	×
撥水性 (°)	92	103	99	98	99	98	89	88	85	75	67	65
耐水性	○	○	○	○	○	○	○	○	○	×	×	×

[0084] In creation example 10 Example 1 of distemper, except having used the following monomeric mixture as a dropped monomeric mixture, it carried out like Example 1 and the colorless, almost translucent water dispersion of 10% of the nonvolatile matter was obtained.

[0085] Styrene Ten copies 48 copies of n-butyl methacrylate Diacetone acrylamide Ten copies Acrylic acid Seven copies KBM-502 15 copies Siliplane FM-0711 Ten copies Azobisisobutyronitrile To the water dispersion obtained one

copy. 5.2 copies of adipic acid dihydrazide was added, it mixed, and the clear coating material was obtained. After painting this by a 50-micrometer applicator to the glass plate and making it dry at 100 °C for 2 hours, when the same system performance testing as the above was presented, paint film appearance and the water resisting property of all were O, and the water contact angle was 93 degrees.

[0086]

[Function and Effect(s) of the invention] In the copolymer solution or the water dispersion of this invention. The alkoxysilyl groups introduced into the copolymer by using a monomer (b) as a copolymerization ingredient hydrolyzes under existence of water, and turns into a silanol group, it can conquer, in order that this silanol group may raise water solubility or water dispersibility remarkably, and it can become possible to lessen the amount of copolymerization of the monomer (c) which has a functional group which moreover gives water solubility/water dispersibility, and water repellence can be raised. In the drying process of the coat by this copolymer solution or a water dispersion, in order to form the firm structure of cross linkage by the self-condensation reaction of silanol groups, the coat which shows a good water resisting property is obtained.

[0087] Therefore, the distemper constituent using the copolymer solution or the water dispersion of this invention as a vehicle component can form the coat excellent in water repellence and a water resisting property.

[Translation done.]

AQUEOUS SOLUTION OR AQUEOUS DISPERSION OF COPOLYMER HAVING
WATER-REPELLING PROPERTY, ITS PRODUCTION AND AQUEOUS COATING
COMPOSITION CONTAINING THE SAME

Publication number JP11124419

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Inventor: MIYATA NAOKI, NUMA NOBUSHIGE

Applicant: KANSAI PAINT CO. LTD.

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Application number: JP19970290018 19971022

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View INPADOC patent family

Abstract of JP11124419

PROBLEM TO BE SOLVED: To obtain the subject aqueous solution useful as a coating resin capable of forming a coating film having excellent water-repellence and water resistance by copolymerizing a mixture containing a monomer having a specific structure, a monomer having an alkoxyethyl group, an ethylenic unsaturated monomer, etc. SOLUTION: The objective aqueous solution is produced by copolymerizing a monomer mixture containing (A) 3-70 wt.% of one or more monomers selected from the monomer of the formula I (R<1> is H or methyl; R<2> is phenyl or a 1-6C alkyl; n<1> is 1-10; n<2> is 5-200) and the formula II (R<3> is H or methyl; X is H or F; n<3> is 1-8; n<4> is 1-30), (B) 1-40 wt.% of a monomer having an alkoxyethyl group, (C) 1-25 wt.% of an α -olefin unsaturated monomer having a functional group selected from carboxyl group, sulfonic acid group and amino group and (D) 0-95 wt.% of other α -olefin, β -ethylenic unsaturated monomers.

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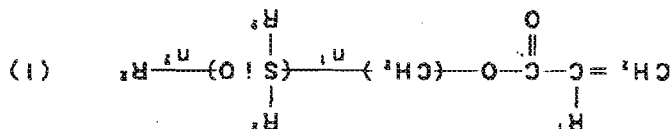
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(21) 出願番号	特願平9-290018	(71) 出願人	000001409 関西ペイント株式会社
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(54) 【発明の名称】 撥水性を有する共重合体水溶液もしくは水分散液、及びその製造方法、及びこれを含む水性塗料組成物

【課題】 撥水性及び耐水性に優れた塗膜を形成し得る塗料用樹脂として有用な共重合体水溶液もしくは水分散液、及びその製造方法、及びこれを含む水性塗料組成物を提供すること。

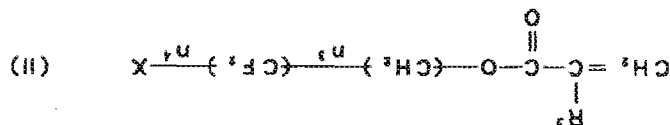
【解決手段】 (a) 2種の撥水性を付与する単量体から選ばれた少なくとも1種の単量体を3〜70重量%、(b) アルコキシシリル基を有する単量体を1〜40重量%、(c) カルボキシ基、スルホン酸基及びアミノ基の群から選ばれた1種の官能基を有する α 、 β -エチレン性不飽和単量体を1〜25重量%、および(d) その他の共重合可能な α 、 β -エチレン性不飽和単量体を0〜95重量%含有する単量体混合物を共重合する。



00の整数を夫々示す。）

【0008】

【化10】



【0007】（式中、R¹は水素原子又はメチル基を、

R²は同一又は異なるフエニル基又は炭素数1～6のアルキル基を、n¹は1～10の整数を、n²は5～2

【0009】（式中、R²は水素原子又はメチル基を、Xは水素原子又はフッ素原子を、n²は1～8の整数を、n¹は1～30の整数を夫々示す。）

(b) アルコキシシリル基を有する単量体を1～40重量%、(c) カルボキシシリル基、アルボキシシリル基及びアミノ

基の群から選ばれた1種の官能基を有するα、β-エチレン性不飽和単量体を1～25重量%、および(d) その他の共重合可能なα、β-エチレン性不飽和単量体を0～95重量%含有する単量体混合物を共重合すること

を特徴とする親水性を有する共重合体水溶液もしくは水

分散液、及びその製造方法、及び該共重合体水溶液もしくは水

分散液を提供するものである。

【0010】

【発明の実施の形態】本発明において上記の構造式

(1) 及び(11)で示される単量体から選ばれた少なくとも1種の単量体(a)は、共重合体に親水性を付与するものであり、上記構造式(1)で示されるポリシロキ

サン鎖を有する単量体(a-1)及び上記構造式(11)で示されるフッ素含有する単量体(a-2)のいずれ

か1方又は両方を使用できる。

【0011】上記構造式(1)で示される単量体(a-1)において、R¹は水素原子またはメチル基であり、R²はフエニル基または炭素数1～6のアルキル基であるが、必ずしも互いに同じものである必要はない、n¹は1～100の整数、n²は5～200、好ましくは15

～150の整数である、n²が5未満では十分な親水性が得られず、逆に200を超える場合は共重合体の親水性が不足し、水溶性もしくは水分散性不良となるので望ましくない、該単量体(a-1)の具体例として、市販

品では、「サイラフレンFM-0711」、「サイラフレンFM-0721」、「サイラフレンFM-0725」(いずれもチソ社製)等が挙げられる。

【0012】上記構造式(11)で示される単量体(a-1)において、R¹は水素原子又はメチル基を、R²は炭素数1～6のアルキル基を、n¹は1～10の整数、n²は5～200、好ましくは15

～150の整数である、n²が5未満では十分な親水性が得られず、逆に200を超える場合は共重合体の親水性が不足し、水溶性もしくは水分散性不良となるので望ましくない、該単量体(a-1)の具体例として、市販

品では、「サイラフレンFM-0711」、「サイラフレンFM-0721」、「サイラフレンFM-0725」(いずれもチソ社製)等が挙げられる。

【0015】（式中、R¹は炭素数1～10のアルキル基を、R²及びR³は同一又は異なるフエニル基、炭素

数1～6のアルキル基又は炭素数1～10のアルコキシ

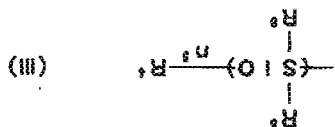
ル基を、n¹は1～4の整数を夫々示す。また、n²が2以上のとき、R²同志及びR³同志は同じであって

も異なっていないよい。）

その代表例として下記構造式(IV)及び(V)で示される単量体を挙げることもできる。

【0016】

【化12】



【化11】

【0014】

コキシシリル基を有するものであり、

【0013】本発明においてアルコキシシリル基を有する単量体(b)は、下記構造式(111)で示されるアル

版有機化学工業社製)などが挙げられる。

コート8FMJ、「ビスコート17FMJ」(いずれも大

品では「FAMAC」(日本マクトロ社製)、「ビス

ルオロシール」エチル(メタ)アクリレートなど、市販

品では「FAMAC」エチル(メタ)アクリレート、2-(メタ

アクリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

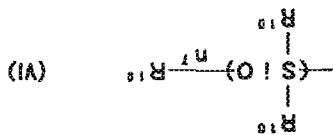
クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

クリレート、2,2,2-トリフルオロエチル(メタ)ア

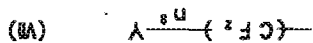
クリレート、2,2,2-トリフルオロエチル(メタ)ア



【0045】(式中、R¹⁰はフェニル基又は炭素数1〜6のアルキル基を、n¹は5〜200の整数を夫々示す。)

【0046】

【化19】



【0047】(式中、Yは水素原子又はフッ素原子を、n²は1〜30の整数を夫々示す。)

【0048】一方本発明では、前記②の製造方法、即ち水を媒体として、これに乳化剤を用いて前記単量体

(a)〜(d)の混合物を分散乳化させ、水溶性の重合開始剤を加えて50〜90℃で加熱することによって行われる乳化重合法をも提供するものである。レゾルス開始剤を用いると室温で行なうことも可能である。乳化剤としては、例えば高級アルコールの硫酸塩、アルキルアルコールの各種アルキルエーテル、アルキルエーテル、アルキルアルコキシエーテルなどの非イオン界面活性剤、及び重合性不飽和基を有する反応性界面活性剤などが使用される。重合開始剤としては、例えば過酸化水素、過硫酸アモモニウム、クメンヒドロパーオキシド、あるいは水溶性レゾルス開始剤などが用いられる。

【0049】次いで本発明では、上記の通り製造される共重合体水溶液もしくは水分散液をビニル成分として含む水性塗料組成物を提供するものである。

【0050】上記共重合体水溶液もしくは水分散液の製造に用いられる単量体(a)〜(d)の混合物には、さらに耐水性などの点からカルボニル基を有する単量体

(e)を、必要に応じて1〜30重量%、好ましくは5〜20重量%含有することができる。

【0051】カルボニル基を有する単量体(e)としては、例えばアクリロイン、ダイアセトペンタクリルアミド、ダイアセトペンタクリルアミド、アセトアセトキシエチルメタクリレート、ホルミルアセトロール、4〜7個

【0038】上記ラジカル重合によって得られた共重合

体(A)を水溶液もしくは水分散する場合、例えば共重合体(A)を水溶液を攪拌しながら中和剤を添加して中和を行なった後、水を添加するか、中和した共重合体(A)を水中に徐々に添加することによって相転換することも可能であるが、この場合アルコキシシリル基の加水分解及び縮合反応が急遽に進行し、増粘、ゲル化することおそれがあるため、それを防止するために中和及び水添加をできるだけ短時間でいうことが望ましい。具体的には、中和剤添加から水による相転換までの時間は、反応容器、攪拌条件、雰囲気温度によって異なるが、一般には24時間以内、好ましくは10時間以内とするのが好都合である。

上記共重合体(A)溶液を、増粘やゲル化させずに水溶液もしくは水分散させる最も好ましい方法は、共重合体(A)溶液に水を添加し、その後中和剤を添加する方法である。この方法によればアルコキシシリル基の加水分解触媒としても作用し架橋を促進する中和剤が水分散後に配合されるので、シラノール基が安定に存在しうることから増粘、ゲル化を防止できる。

【0039】また本発明方法においては、共重合体(A)溶液に、親水性基を含まない水溶液もしくは水分散可能な樹脂(B)溶液を混合してから、該混合物に水および中和剤を添加して水溶液もしくは水分散化して製造することができる。

【0040】該樹脂(B)としては、共重合体(A)と十分混合するものであれば特に制限はなく、例えば水溶性/水分散性を付与する単量体及びその他の単量体を共重合することにより得られる共重合体、具体的には前記単量体(c)及び単量体(b)、(d)に列記の中から適宜選択して共重合することにより得られる共重合体を

使用することができる。共重合反応は共重合体(A)と同様に進行することができる。

【0041】上記樹脂(B)を用いる場合、樹脂(B)の使用割合は、共重合体(A)との合計樹脂固形分中に95重量%以下、好ましくは80重量%以下となるようにする。増粘剤(9)の使用割合が95重量%を超えると十分な親水性を得られない場合があるのを望ましくない。

【0042】さらに本発明方法において、上記共重合体(A)の水溶液もしくは水分散化に際して特に塗膜形成初期の親水性を向上させる目的で、共重合体(A)溶液もしくは共重合体(A)及び樹脂(B)の混合溶液に親水性基を有する界面活性剤を添加して水溶液もしくは水分散化することができる。

【0043】該界面活性剤としては、例えば下記構造式(VI)または(VII)で示される親水性基を有するものが使用できる。

【化18】

【0044】

【0045】

の炭素原子を有するビニルアルキルケン（例えばビニルメチルケン、ビニルエチルケン、ビニルプロピルケン）等が挙げられる。このうち特にダイアセトペンタリルアミン、ダイアセトペンタリルアミンが好適であ

【0052】本発明の水性塗料組成物は、上記カルボニル基が共重合体に導入された場合には、架橋剤として、1分子中に少なくとも2個の-NH-NH₂含有基を有するビニル誘導体を含有することができる。ここで

-NH-NH₂含有基には、ヒドラジド基、セミカルバ

ジド基が含まれる。

【0053】該ヒドラジド誘導体としては、例えば脛酸ジヒドラジド、プロン酸ジヒドラジド、グルタル酸ジヒドラジド、セバシン酸ジヒドラジド等の2～18個の炭素原子を有する飽和脂肪族カルボン酸ジヒドラジド；アレイ

ン酸ジヒドラジド、フタル酸ジヒドラジド、イタコン酸ジヒドラジド等のモノオレフィン性不飽和カルボン酸ジヒドラジド；フタル酸、チレフタル酸またはイソフタル酸ジヒドラジド、ならびにピロキリッ酸のジヒドラジド、トリヒドラジドまたはテトラヒドラジド；ニトリ

ロトリヒドラジド、クエン酸トリヒドラジド、1,2,4-ベンゼントリヒドラジド、エチレンジアミンチトラジヒドラジド、カルボキシ低級アルキルエチル基を有する低重合体をヒドラジドまたはヒドラジド水化合物

（ヒドラジドヒドラジド）と反応させてなるポリヒドラジド（特公昭52-22878号参照）；脛酸ジヒドラジド、ヒスセミカルバジド；ヘキサメチレンジアジド、ネートやイソプロピルアミン等のジイソシアネート及びそれより誘導されるポリイソシアネート化合物

スチレン

メタクリル酸n-ブチル

アクリル酸

KBM-502（注1）

サイラアレンFM-0711

アビエスアノブチロニトリル

その後還流温度に保ちながら2時間熟成した後室温まで冷却し、不揮発分5.6%のほぼ無色透明の粘稠な共重合

体溶液を得た。続いて得られた共重合体溶液を希釈槽に移し、酢酸イソブチル82.0部、続いてトリエチルアミン9.8部を加えて50℃に昇温したのち、温度を50℃に保ちながら2時間攪拌を行ってから冷却し、不揮発分10%のほぼ無色の半透明な水分散液を得た。

【0059】（注1）KBM-502：信越化学工業社製、アルコキシシリル基含有単量体、

スチレン

メタクリル酸n-ブチル

アクリル酸

ビニルトリメチルシリル

にヒドラジド化合物や上記例示のジヒドラジドを過剰に反応させて得られる多官能セミカルバジド、該ポリイソシアネート化合物とポリエーテルポリオール類やポリエチレングリコールモノアルキルエーテル類等の親水性基を含む活性水素化合物との反応物中のイソシアネート基を上記例示のジヒドラジドを過剰に反応させて得られる多官能セミカルバジド、或いは該多官能セミカルバジドと水素多官能セミカルバジドとの混合物（特開平8-151358号、特開平8-245878号参照）等が挙げられる。

【0054】該ヒドラジド誘導体は、前記共重合体水溶液もしくは水分散液中に含まれるカルボニル基の1モルに対してヒドラジド誘導体中の-NH-NH₂基が0.01～2モル、好ましくは0.05～1.5モルとなるように配合される。

【0055】本発明の水性塗料組成物には、さらに必要に応じて、顔料、充填剤、骨材、顔料分散剤、湿潤剤、消泡剤、可塑剤、造膜助剤、有機溶剤、防曇剤、防かび剤、pH調整剤、防錆剤、硬化触媒などの塗料用添加剤を適宜選択し組合わせて配合することができる。

【0056】以下、実施例を挙げて本発明をさらに詳細に説明する。「部」及び「%」はそれぞれ「重量部」及び「重量%」を意味する。

【0057】共重合体水分散液の製造

実施例1
フラスコ中にイソプロピルアルコール79重量部を仕込み、還流温度（約84℃）まで攪拌を行いながら昇温した。次いで温度を還流温度に保ちながら下記単量体混合物を4時間滴下した。

10部

5.8部

7部

1.5部

10部

1部

（注2）サイラアレンFM-0711：チソ社製、ポリジメチルシロキサン基含有単量体、分子量1,000
実施例2
実施例1において、滴下する単量体混合物として下記の単量体混合物を用いた以外は実施例1と同様にして行い、不揮発分10%のうすい乳白色の水分散液を得た。

【0060】

10部

2.8部

7部

1.5部

【0061】
い、不揮発分10%のうすい乳白色の水分散液を得た。
40部
1部

【注4】
10部
58部
7部
15部
10部
1部

実施例4
実施例1において、滴下する単量体混合物として下記の
単量体混合物を用いた以外は実施例1と同様にして行
い、不揮発分10%のうすい乳白色の水分散液を得た。
【0062】

10部
62部
7部
10部
10部
10部
1部

ラスコ中で重合反応を行い、不揮発分56%のほぼ無色
透明の粘潤な共重合体溶液を得た。続いて得られた樹脂
溶液を希釈槽に移し、「フロラ-FC-93」（住友
スリーエム社製、フッ素系界面活性剤）0.15部を添
加して10分間攪拌した。その後脱イオン水820部、
続いてトリエチルアミン9.8部を加えて50℃に昇温
したのち温度を50℃に保ちながら2時間攪拌を行って
から冷却し、不揮発分10%のほぼ無色の半透明な水分
散液を得た。
【0064】実施例7

フラスコ中にイソプロピルアルコール79重量部を仕込
み、還流温度（約84℃）まで攪拌を行いながら昇温し
た。次いで温度を還流温度に保ちながら下記単量体混合
物を4時間滴下した。
【0065】

10部
30部
10部
5部
10部
35部
1部

液（A）と同様にして重合反応を行い、不揮発分56%
のほぼ無色透明の粘潤な共重合体溶液（B）を得た。
【0066】

5部
26部

サイラアレン-PM-0711
アノビスイソチロニトリル

実施例3
実施例1において、滴下する単量体混合物として下記の
単量体混合物を用いた以外は実施例1と同様にして行

アチレン

メタクリル酸n-ブチル

アクリル酸

KBM-503（注3）

サイラアレン-PM-0725

アノビスイソチロニトリル

（注3）KBM-503：信越化学工業社製、アルコキ
シシリル基含有単量体、

（注4）サイラアレン-PM-0725：チッソ社製、
ポリジメチルシロキサン基含有単量体、分子量10,000

アチレン

メタクリル酸n-ブチル

アクリル酸

KBM-502

FAMAC（注5）

アノビスイソチロニトリル

（注5）FAMAC：日本メクトロン社製、パ-フルオ
ロアルキルメタクリレート、フッ素濃度60.7重量%

実施例5

実施例1と同様の単量体混合物を用いて同様の操作でフ
ラスコ中で重合反応を行い、不揮発分56%のほぼ無色

透明の粘潤な共重合体溶液を得た。続いて得られた樹脂
溶液を希釈槽に移し、「KF-355」（信越化学工業

社製、シリコン系界面活性剤）0.4部を添加して10分間攪拌した。その後脱イオン水820部、続いてトリエチルアミン9.8部を加えて50℃に昇温したのち温度を50℃に保ちながら2時間攪拌を行ってから冷却し、不揮発分10%のほぼ無色の半透明な水分散液を得た。
【0063】実施例6

実施例1と同様の単量体混合物を用いて同様の操作でフ
ラスコ中で重合反応を行い、不揮発分56%のほぼ無色
透明の粘潤な共重合体溶液を得た。続いて得られた樹脂
溶液を希釈槽に移し、「KF-355」（信越化学工業
社製、シリコン系界面活性剤）0.4部を添加して10分間攪拌した。その後脱イオン水820部、続いてトリエチルアミン9.8部を加えて50℃に昇温したのち温度を50℃に保ちながら2時間攪拌を行ってから冷却し、不揮発分10%のほぼ無色の半透明な水分散液を得た。
【0063】実施例6

アチレン

メタクリル酸n-ブチル

メタクリル酸メチル

アクリル酸

KBM-502

サイラアレン-PM-0711

アノビスイソチロニトリル

その後還流温度に保ちながら2時間加熱した後室温まで
冷却し、不揮発分56%のほぼ無色透明の粘潤な共重合
体溶液（A）を得た。別フラスコにおいて、滴下する単
量体混合物として下記混合物を用いた以外は共重合体混

アチレン

メタクリル酸n-ブチル

メタクリル酸メチル

アクリル酸2-ヒドロキシエチル

アクリル酸

KBM-502

アビエスノブチロニトリル

上記のように得られた共重合体溶液(A)18部、及び

共重合体溶液(B)162部を希釈槽に夫々仕込み、1

5分間攪拌してから、脱イオン水816、5部、続いて

トリエチルアミン13、3部を加えて50℃に昇温した

のち温度を50℃に保ちながら2時間攪拌を行ってから

冷却し、不揮発分10%の乳白色の水分散液を得た。

【0067】実施例8

実施例1と同様の単量体混合物を用いて同様の操作でフ

メタクリル酸n-ブチル

メタクリル酸メチル

アクリル酸

アビエスノブチロニトリル

上記のように得られた共重合体溶液(C)108部、及

び共重合体溶液(D)72部を希釈槽に夫々仕込み、1

5分間攪拌してから、脱イオン水807、1部、続いて

トリエチルアミン22、7部を加えて50℃に昇温した

のち温度を50℃に保ちながら2時間攪拌を行ってから

冷却し、不揮発分10%のほぼ無色透明な水分散液を得

【0070】実施例9

フラスコ中にアビエスノブチロニトリル

メタクリル酸n-ブチル

メタクリル酸n-ブチル

アクリル酸2-ヒドロキシエチル

アクリル酸

サイラアレーンFM-0711

KBM-503

アビエスノブチロニトリル

上記のように得られた共重合体溶液(A)108部、及

び共重合体溶液(B)72部を希釈槽に夫々仕込み、1

5分間攪拌してから、脱イオン水807、1部、続いて

トリエチルアミン22、7部を加えて50℃に昇温した

のち温度を50℃に保ちながら2時間攪拌を行ってから

冷却し、不揮発分10%のほぼ無色透明な水分散液を得

比較例1

実施例1において、滴下する単量体混合物として下記の

単量体混合物を用いた以外は実施例1と同様にして行

アクリル酸

サイラアレーンFM-0725

アビエスノブチロニトリル

実施例1において、滴下する単量体混合物として下記の

10部

73部

7部

10部

実施例1において、滴下する単量体混合物として下記の

比較例3

アビエスノブチロニトリル

FAMAC

アクリル酸

メタクリル酸n-ブチル

アクリル酸

アビエスノブチロニトリル

実施例1において、滴下する単量体混合物として下記の

10部

73部

7部

10部

実施例1において、滴下する単量体混合物として下記の

10部

73部

7部

10部

実施例1において、滴下する単量体混合物として下記の

単量体混合物を用いた以外は実施例1と同様の操作でフラスコ中で重合反応を行い、不揮発分5.6%のほぼ無色

【0074】
 透明の粘潤な共重合体溶液を得た。
 実施例1において、滴下する単量体混合物として下記の単量体混合物を用いた以外は実施例1と同様にして行い、不揮発分1.0%のほぼ無色の半透明な水分散液を得た。
 【0076】
 単量体混合物を用いた以外は実施例1と同様の操作でフラスコ中にエチレンジトリコールモノアチルエーテル7.0重量部を仕込み、95℃まで攪拌を行いながら昇温し

【0075】比較例4
 スチレン
 メタクリル酸n-アチル
 メタクリル酸メチル
 アクリル酸
 KBM-502
 アビエスイソチクロニトリル

【0077】
 4.2、5部
 1.2、5部
 1.5部
 3.0部
 0.7部

【0077】
 4.2、5部
 1.2、5部
 1.5部
 3.0部
 0.7部

【0079】
 0.15部と脱イオン水9.5部を仕込み、85℃に昇温した。続いて下記の単量体混合物を水8.0部にホモキサールを用いて分散してから過硫酸アモニウム1.0部を添加した。その水分散液を5時間かけてフラスコ中に滴下し、さらに2時間熱成させて不揮発分3.9%の乳白色のエマルションを得た。得られたエマルションは脱イオン水で不揮発分1.0%に希釈して性能試験に用いた。
 【0079】

【0082】(*3) 耐水性：各塗装板を20℃の上水に6時間没水した後、塗面に異常のないものを○、白化やフクレが認められるものを×とした。
 【0083】
 【表1】

性能試験
 上記の通り得られた実施例1～9および比較例3～6の水分散液もしくは水溶液は、いずれも良好な水分散性を示しており、これらをガラス板に50μmアクリターで夫々塗装し、100℃で2時間乾燥させた後、下記【0080】(*1) 塗膜外觀：目視で評価し、良好なものを○、ツヤびけが認められるものを×とした。
 【0081】(*2) 耐水性：各塗装板上に0.03cc

表1

比較例	実施例										塗膜外観	撥水性(°)	耐水性
	1	2	3	4	5	6	7	8	9	10			
	○	○	○	○	○	○	○	○	○	○	○	92	○
	2	3	4	5	6	7	8	9	10	11	○	103	○
	1	2	3	4	5	6	7	8	9	10	○	99	○
	1	2	3	4	5	6	7	8	9	10	○	93	○
	1	2	3	4	5	6	7	8	9	10	○	98	○
	1	2	3	4	5	6	7	8	9	10	○	88	○
	1	2	3	4	5	6	7	8	9	10	○	85	○
	1	2	3	4	5	6	7	8	9	10	○	75	○
	1	2	3	4	5	6	7	8	9	10	○	67	○
	1	2	3	4	5	6	7	8	9	10	○	65	○
	1	2	3	4	5	6	7	8	9	10	×	77	×

【0084】水性塗料の作成

実施例10

実施例1において、滴下する単量体混合物として下記の

単量体混合物を用いた以外は実施例1と同様にして行

なした。

【0085】

イ、不揮発分10%のほぼ無色の半透明な水分散液を得

る。

【0086】

【作用及び発明の効果】本発明の共重合体水溶液もしく

は水分散液では、単量体(a)により導入された親水性

基による水溶性、水分散の難しさを、単量体(b)を共

重合成分とすること共重合体中に導入されたアルコキ

シシリル基が水の存在下で加水分解してシラノール基と

なる。

【0087】従って本発明の共重合体水溶液もしくは水

分散液をビニル成分として用いた水性塗料組成物は、

親水性及び耐水性に優れた塗膜を形成することができ

る。

【0088】

【0089】

【0090】

【0091】

【0092】

【0093】

【0094】

【0095】

【0096】

【0097】

【0098】

【0099】

【0100】

【0101】

【0102】

【0103】

【0104】

【0105】

【0106】

【0107】

【0108】

【0109】

【0110】

【0111】

【0112】

【0113】

【0114】

【0115】

【0116】

【0117】

【0118】

【0119】

【0120】